

**THE EFFECT OF VACUUM PRESSURE ON THE FLAMMABILITY
LIMITS OF HYDROGEN (H₂) ENRICHED LIQUEFIED PETROLEUM GAS
(LPG) IN A CLOSED VESSEL**

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ABSTACT

An experimental study on pressure explosion in 20-L closed vessel explosion unit of LPG–air –hydrogen mixtures was performed, for systems with various pressures evacuated. The objective of this research is to determine the correlation of vacuum pressure toward flammability limits of LPG H₂ enriched. The explosion pressures and explosion times were measured in a 20-L closed vessel, at ambient initial temperature. The influence of initial pressure, initial temperature and fuel concentration on explosion pressures and explosion times are discussed. The explosion pressure data is use to determine the flammability limits of hydrogen enriched LPG. From the result, there are fairly same in flammability limits of LPG but there are quiet different in maximum pressure explosion which is increasing the pressure can be decrease the value of pressure explosion. Increasing vacuum pressure from 0.02 bar up to 0.04 bar slightly increase the upper flammability limit from 8.2 % to 8.3 % volume of liquefied petroleum gas by volume and also decrease the maximum pressure explosion which is from 5.8 bar to 5.7 bar.

ABSTRAK

Kajian eksperimen dilakukan ke atas tekanan letupan dalam 20 liter bekas tertutup unit letupan terhadap campuran gas petroleum cecair, udara dan gas hydrogen dengan pelbagai nilai tekanan yang disalurkan ke dalam unit tersebut. Objektif kajian ini ialah untuk mencari perhubungan antara tekanan vakum terhadap limit pembakaran gas petroleum cecair yang mengandungi gas hydrogen. Tekanan dan masa letupan di dalam 20 liter bekas tertutup diambil kira pada suhu persekitaran. Pengaruh tekanan dan suhu awal serta kepekatan gas terhadap tekanan dan masa letupan dibincangkan. Data dari tekanan letupan ini digunakan untuk mendapatkan nilai limit pembakaran bagi gas petroleum cecair yang mengandungi gas hydrogen. Daripada keputusan yang diperolehi mendapati bahawa tidak banyak perubahan yang berlaku terhadap limit pembakaran tetapi perubahan jelas kelihatan pada maksimum tekanan letupan di mana bila tekanan vakum ditambah ia akan mengurangkan tekanan letupan di bekas tertutup unit letupan tersebut. Bilamana tekanan vakum dinaikkan dari 0.02 bar kepada 0.04 bar, terdapat sedikit perubahan pada limit bahagian atas bagi tekanan letupan yang mana terdapat sedikit kenaikan iaitu dari 8.2 % ke 8.3 % isipadu gas petroleum cecair dan dapat mengurangkan maksimum tekanan letupan iaitu dari 5.8 kepada 5.7 bar.

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LIST OF ABBREVIATIONS

LPG	-	Liquefied Petroleum Gas
UFL	-	Upper Flammability Limits
LFL	-	Lower Flammability Limits
H ₂	-	Hydrogen Gas
HC	-	Hydrocarbon
CO	-	Carbon Monoxide
NO _x	-	Nitrous Oxide
IE		Ignition Energy
P _{max}	-	Maximum Explosion Overpressure
Kg	-	Deflagration Index
MOC	-	Maximum Oxygen Concentration
P _m	-	Explosion Overpressure
P _{vac}	-	Vacuum Pressure

CHAPTER 1

INTRODUCTION

1.1 Introduction

Knowledge of pressure–time variation during explosions of fuel–air mixtures in enclosures is a very important component of safety recommendations for a wide range of human activities, connected to production, transportation or use of fuels (Domnina Razus et al, 2005).

Actually liquefied Petroleum gas (LPG) is the most dangerous fuel that is made from petroleum since its specific gravity is greater than air which can easily form vapor cloud that might cause explosion. By the way, LPG is much needed now a day as a fuel of transportation and generates power for some industry. Recent studies on internal combustion engines with hydrogen enriched fuels showed that hydrogen addition could increase the engine thermal efficiency, improve the lean burn capability and mitigate the global warming problem (Van Blarigan P, Keller JO, 1998).

There are two categories of limits or range for the flammability or explosion of mixture to occur, which lower flammability limit (LFL) and upper flammability limit (UFL). Within UFL and LFL the explosion will occur if there are mixed of fuel and air.

In many practical applications for power generation, such as gas turbines, there has been strong interest in achieving lean premixed combustion because nowadays people started to aware about safety and environment besides concern about the efficiency of the operation (Ramanan and Hong, 1994)

1.2 Problem Statement

Since there are many incidents happen in industry especially while handling LPG is due to the related to the pressure especially in LPG pipeline and storage installation. LPG is the most dangerous substance of fuel. There is range of pressure that need to consider while running the project or experiment to ensure that it is in a safe condition. While using closed vessel of explosion unit, the vacuum pressure can ensure the safety of LPG measurement.

Other than that, LPG is the most wanted fuel nowadays and environmental friendly. Recent studies on internal combustion engines with hydrogen enriched LPG showed that hydrogen addition could increase the engine thermal efficiency, improve the lean burn capability and mitigate the global warming problem. (Chenglong Tang et al, 2008)

1.3 Objective

The objectives of this study are:

- a) To determine the effect of vacuum pressure on the flammability limits of H₂ enriched LPG.
- b) To determine the flammability limits of H₂ enriched LPG in explosion unit.

1.4 Scope of Study

1. The used equipment in this experiment is explosion unit. Using a spherical 20 L closed vessel with central ignition, produced by a fusing wire, a pyrotechnical ignitor or capacitive electric sparks.
2. In this study, butane and propane with 70 % and 30 % purity is used to investigate the explosive limits.
3. The LFL and UFL of LPG-air mixture are determined at concentration from 1 vol % to 8 vol %.
4. This analysis is operating vacuum pressure condition where at pressure 0.02 bar and 0.04 bar and at room temperature, 25°C.
5. Generally this experimental are operating to determine the effect of vacuum pressure on the flammability limits of H₂ enriched LPG.

1.5 Rationale and Significance

In this study, the effect of vacuum pressure in LPG-air-hydrogen mixtures is investigated in closed vessel. Addition of vacuum pressure is said can extend the flammability limits of LPG-air-hydrogen mixture and minimize the pressure explosion.

The rationale of this research is to ensure the safety measurement while handling LPG which is consequently related to pressure. The vacuum pressure in closed vessel is related to the explosion pressure which is important in safety measurement. The limits of flammable of LPG can be found from the explosion pressure. Within the range of the flammable limits, explosion will be happened.

The pollution levels recorded in large urban areas are raising concern for public health and substantial reductions in pollutant emissions have become an important issue (Heywood and John, 1988). From an environmental point of view there is an increasing interest among the suppliers to investigate LPG as butane, which gives a benefit in terms of toxic hydrocarbons emissions and ozone formation due to its composition and CO₂ emission levels (Haffer, 2003). Karim *et al* (1996) described that the hydrogen is the primary fuel options under consideration for fuel cell vehicles. The ideal fuel would eliminate local air pollution, reduce greenhouse gas emissions and oil imports (Kim *et al.*, 1999)

CHAPTER 2

LITERATURE REVIEW

2.1 Vacuum Pressure

By definition vacuum is a space that is partially exhausted (as to the highest degree possible) by artificial means (as an air pump). This definition is referring to a high or hard vacuum. Figure 2.1.1 illustrates that relationship of absolute and gage pressure with 0 psia equal to a high or hard vacuum.

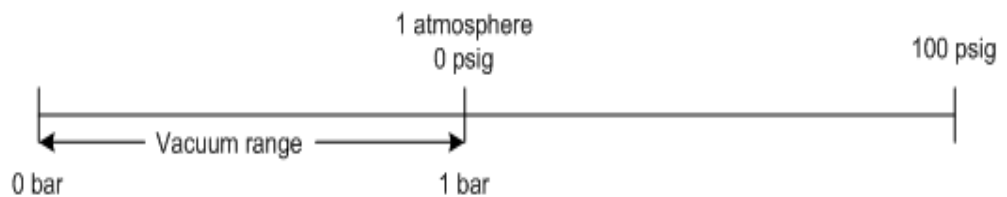


Figure 2.1.1

From figure 2.1.1, vacuum can refer to any pressure between 0 psia and 14.7 psia (0 – 1 bar) and consequently must be further defined. For applications concerned with measuring vacuum pressures over this full range two different

approaches are often taken. Figure 2.1.2 illustrates the relationship of absolute and vacuum pressures.



Figure 2.1.2

Vacuum pressure is measured relative to ambient atmospheric pressure.

2.2 Flammability Limits

Flammability limits, also called flammable limits, or *explosive limits* give the proportion of combustible gases in a mixture, between which limits this mixture is flammable. Flammability limit can be divided into two categories which is upper flammability limit (UFL) and lower flammability limit (LFL).

The explosion limit of gas mixtures, which is defined as the fuel concentration between the lower and the upper explosion limit in air or other oxidiser at given conditions, is a very important parameter in risk studies and safe design. If an industrial process operates outside a well-defined explosion limit, under normal operation conditions, the flame, even if ignited, cannot propagate. Therefore, in these conditions, an explosion cannot occur. While accurate determination of the explosion limit for a given method, conditions and criteria require only accurate instruments and careful experimenting and observation, the proper determination is more complex. The complexity arises from experimental factors, which influence the value of the explosion limits and proper interpretation of observed phenomena. Factors are initial pressure, initial temperature, size of an experimental vessel and its dimensions, ignition type and

energy, direction of flame propagation, turbulence, presence of impurities, and ignition criterion. Additionally, at elevated conditions, the state of the vessel walls (heterogeneous reactions), pre-ignition reactions, cool flame phenomena and multi-stage ignition in general contribute to the complexity (Pekalski et al., 2002 and Pekalski et al., 2005).

There are two distinct separate flammability limits for a mixture which are lean limit or lower flammability limit (LFL) and rich limit or upper flammability limit (UFL).

- i. Above the upper flammable limit (UFL) the mixture of substance and air is too rich in fuel (deficient in oxygen) to burn. This is sometimes called the upper explosive limit (UEL).
- ii. Below the lower flammable limit (LFL) the mixture of substance and air lacks sufficient fuel (substance) to burn. This is sometimes called the lower explosive limit (LEL).

In other words, combustion or explosion will take place and be self-sustaining only if fuel and air are mixed within the upper and lower flammability limits (Liao, 2005).

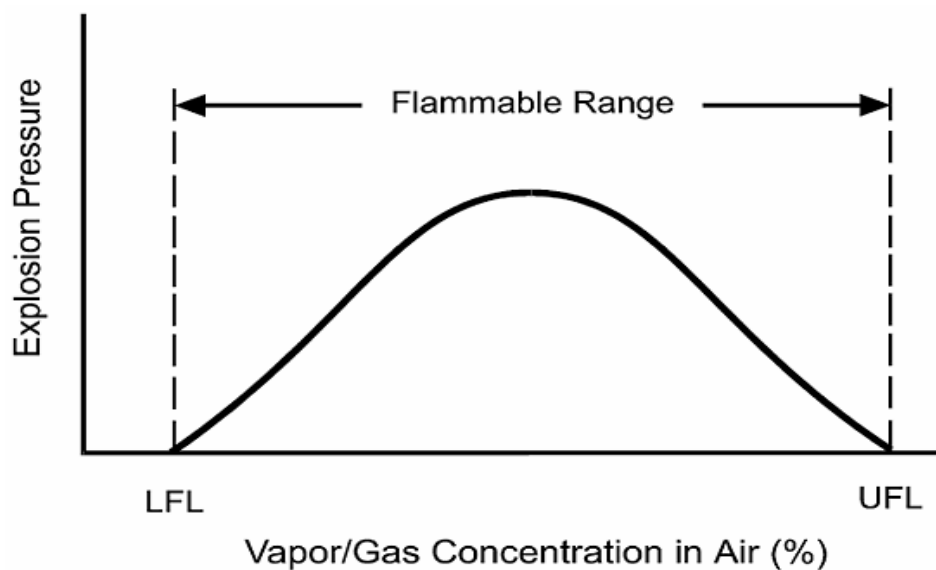


Figure 2.2 Schematic represents flammability limit

The determination of the upper explosion limit is much more problematic than that of the lower one. The lower one is usually a rather sharp cut-off also at elevated conditions. It also does not shift much with higher pressure and temperature. This does not mean there is no ambiguity about its value. However the dispersion in values leaves less uncertainty than for the upper explosion limit. The latter also shifts over a wide range to higher fuel composition with both pressure and temperature (Holtappels et al., 2007). However, depending on the nature of the fuel over a considerable part of the range adjacent to the limit, the severity of the explosion in terms of explosion pressure and rate of pressure rise of the explosion is very low. This means that also the risk of obtaining damage to equipment is low.

When increasing temperature in a given mixture, which is in the explosion limits, the possibility of self-ignition will come closer. At higher pressure self-ignition will even occur easier. It means that with limit compositions at higher pressure and higher temperature a self-ignition threshold is reached beyond which a mixture self-ignites after a certain induction period. Self-ignition will start at the hottest spot. If induction is sufficient short a flame ball may expand in the reacting mixture. On the other hand if induction is relatively long the reacting mixture may well be exhausted and no flame ball will develop. In such case the mixture is beyond the explosion limit but is still reactive and can develop heat, which in a closed vessel will lead to pressure increase.

2.3 Experimental Method

The standardized measurements of flammability limits are usually conducted in flammability tubes or closed vessels. There are several criteria to determine the flammability limits. A successful attempt can be determined by one or a combination of the following criteria:

1. Inspection of the visualization of the flame kernel produced by spark, namely visual criterion.
2. Measurements of pressure or temperature histories in the vessel and appropriate pressure or temperature rise criteria can be used to designate flammability rather than the purely visual observation of flame development.

A successful ignition would induce a rapid pressure increase and temperature within a short time as well as produce a propagating flame front that could be readily observed.

Previous gas flammability limit data were obtained mainly in flammability tubes which those tests a gas mixture in vertical tube was ignited and flame propagation was inspected by visual criterion. However, the wall quenching has a significant effect on the flammability measurement in flammability tube.

Recently, the flammability measurement is conducted in closed vessels. This is because the large size of combustion vessel can minimize wall effects and can allow potential use of stronger igniters to ensure the absence of ignition limitations (Jiang *et al.*, 2005)

2.4 Liquefied Petroleum Gas

Liquefied petroleum gas (LPG) is defined as a petroleum product composed predominantly of any of the following hydrocarbons or mixtures thereof: propane, propylene, butanes (normal butane or isobutane), and butylenes. These substances are generally extracted from natural gas or produced as a byproduct of the refining of crude oil.

Liquefied Petroleum gas (LPG) is gaseous under normal atmospheric conditions, but liquefied by cooling and/or compression. LPG is commonly used as an industrial fuel for domestic and commercial purposes like town gas and autogas. LPG is also used as feedstock in chemicals plant processes.

2.4.1 Liquefied Petroleum Gas Properties

Table 2.4.1: Properties of Propane and Butane

Properties of		Propane	Butane
Chemical formula		C_3H_8	C_4H_{10}
Boiling point of liquid at atmospheric pressure	°C	-42	0
Specific Gravity of vapor (Air = 1)		1.53	2.00
Specific Gravity of liquid (Water = 1)		0.51	0.58
Calorific value @ 15°C	BTU/gal	91690	102,032
Latent heat of vaporization	BTU/gal	785	808
Liquid weight	kg/liter	0.508	0.576
Vapor volume from 1 liter of liquid at 15°C	m ³	0.272	0.234
Vapor volume from 1 kg of liquid at 15°C	m ³	0.534	0.406
Combustible limits	% of gas in air	2.4-9.6	1.9-8.6

Amount of air required to burn 1 m ³ of gas	m ³	23.86	31.02
Ignition temperature	°C	490-550	480-540
Maximum flame temperature in air	°C	1980	1991
Octane Number		Over 100	92

2.5 Hydrogen Enriched Liquefied Petroleum Gas

Increasing concern over the fossil fuel shortage and air pollution has intensified the study on the alternative fuels around the world. Propane, which is the major component of liquid petroleum gas, has good air–fuel mixing potential and hence low HC and CO emissions. Propane can be pressurized into the liquid state under a moderate pressure, and this makes the onboard storage and handling easier (Yap et al, 2005). Hydrogen has high flame speed, wide flammability range, low minimum ignition energy, and free carbon-related emissions (Wang ,2008). It is considered as one of the most promising alternative fuels for engines. However, hydrogen fueled engine are prone to pre-ignition and could potentially emit high levels of NO_x (Mohammadi et al,2007).

Hydrogen and other fuel combination is one of the effective approaches in utilization of hydrogen for clean combustion. Recent studies on internal combustion engines with hydrogen enriched fuels showed that hydrogen addition could increase the engine thermal efficiency, improve the lean burn capability and mitigate the global warming problem (Saravanan and Nagarajan, 2008) Fundamental combustion studies of propane –air (Tseng et al,1993) and hydrogen–air (Aung et al, 1997) mixtures have been extensively studied. However, few reports on combustion of hydrogen- enriched propane –air flames were presented. Milton and Keck (Milton and Keck,1984) measured the laminar burning velocities of the stoichiometric hydrogen– propane –air flames. Yu, Law and Wu studied the laminar burning characteristics of propane –

hydrogen–air flames with the assumption that the stoichiometrically small amounts of hydrogen in the mixture was completely consumed and a linear correlation of laminar burning velocity to hydrogen concentration was summarized.

Law and Kwon studied the potential of hydrocarbon addition to suppress explosion hazards and found that a small or moderate amount of propane addition could remarkably reduce the laminar burning velocities and would suppress the propensity of onset of both diffusional-thermal and hydrodynamic cellular instabilities in hydrogen–air flames. Law et al. investigated the phenomenon of spontaneous cell formation on expanding lean hydrogen spherical flames with propane addition to retard the reaction intensity and they found that the critical radius at the onset of instability would increase with the increase of propane fraction.

2.6 Explosion Pressure

Knowledge of pressure-time variation during explosion of fuel-air mixtures in enclosures is a very important of safety recommendations for wide range human activities, connected to production, transportation or use fuels.

The characteristic parameters of a closed vessel explosion are the explosion pressure, explosion time and the maximum rate of explosion rise. The explosion pressure and explosion time were recently defined in the European standard on maximum explosion pressure determination:

1. The explosion pressure is the highest pressure reached during the explosion in a closed volume at a given fuel concentration.
2. The maximum explosion pressure is the highest pressure reached during a series of explosions of mixtures with varying fuel concentration.

3. The explosion time is the time interval between ignition time and the moment when the explosion pressure attained.

Explosion pressures and explosion times are important for calculating laminar burning velocities from closed vessel experiments, vent area design, and characterizing transmission of explosion between interconnected vessels (Razus *et al.*, 2006).

2.7 20-L-Spherical Explosion Vessel

The experimental 20-L-Apparatus (or 20 Liter Spherical Explosion Vessel) was obtained from Adolf Kühner AG and is shown in figure 3.1. The test chamber is stainless steel hollow sphere with personal computer interface. The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap which is controlled by the KSEP 310 unit of the 20-L-Apparatus. The KSEP 332 unit uses piezoelectric pressure sensors to measure the pressure as function of time (ASTM, 1991; Operating Instructions for the 20-L-Apparatus, 2006). A comprehensive software package KSEP 5.0 is available, which allows safe operation of the test equipment and an optimum evaluation of the explosion test results.

In the past, the international standards have described the 1 m³ vessel as the standard test apparatus. In recent years, increased use has been made of the more convenient and less expensive 20-L-Apparatus as the standard equipment. The explosion behavior of combustible materials (combustible dusts, flammable gases, or solvent vapours) must be investigated in accordance with internationally recognized test procedures. For the determination of combustible

gases or vapours the test is generally accomplished in a quiescent state (ignition delay time, $t_v = 0$ sec) (Operating Instruction for the 20-L-Apparatus, 2006).

In the 20-L-Apparatus, important explosion characteristics of gases and vapours, such as explosive limits, maximum explosion overpressure (P_{\max}), gas or vapour deflagration index (K_g), and maximum oxygen concentration (MOC), can be determined with adherence to standardized test procedures.

CHAPTER 3

METHODOLOGY

3.1 Experimental Apparatus

The experimental 20 L Apparatus or 20 litre Spherical Explosion Vessel was obtained from Adolf Kühner AG and is shown in Fig. 3.1. The test chamber is a stainless steel hollow sphere with a volume of 20 liter. The ignition sources are located in the center of the sphere. On the measuring flange two “Kistler” piezoelectric pressure sensors are installed. The second flange can be used for additional measuring elements or for the installation of a sight glass.

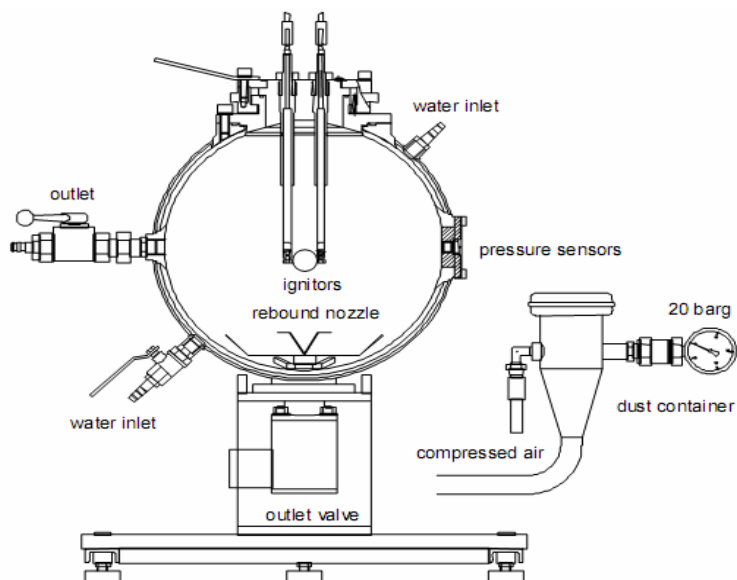


Figure 3.1 Schematic diagram of 20-L-Apparatus

3.1.1 20-L-Apparatus

The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition which controlled by the KSEP 320 units of 20 L Apparatus. The KSEP 332 unit uses piezoelectric pressure sensor's to measure the pressure as a function of time. A comprehensive software package KSEP 6.0 is used to allow safe operation of the test equipment and an optimum evaluation of the explosion test results as shown in Figure 3.1.1.